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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : C08F 297/04, C09J 153/02, B32B 27/28 — A1

(11) International Publication Number: WO 00/56796

(43) International Publication Date: 28 September 2000 (28.09.00)

(21) International Application Number: PCT/US00/08012

(22) International Filing Date: 24 March 2000 (24.03.00)

(30) Priority Data:
09/276,009 25 March 1999 (25.03.99) US

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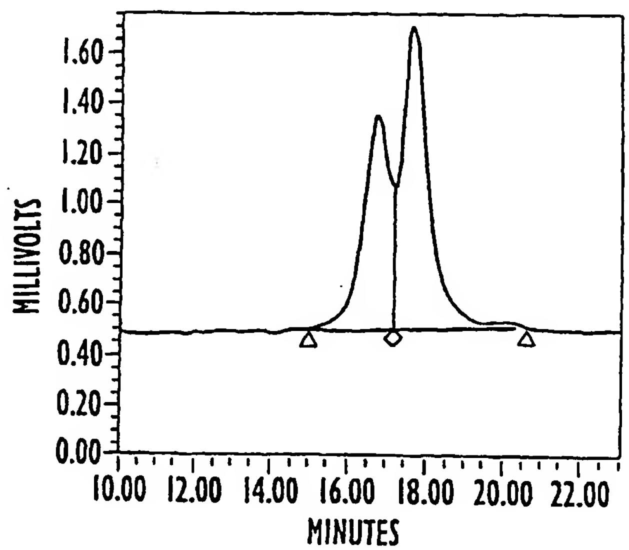
(81) Designated States: JP, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: ADHESIVE COMPOSITIONS CONTAINING MULTIBLOCK POLYISOPRENE-POLYSTYRENE COPOLYMERS AND ARTICLES INCLUDING SAME

(57) Abstract

Multiblock polyisoprene–polystyrene copolymers can be used with tackifier resins, plasticizer oil and antioxidants to formulate hot melt, pressure sensitive adhesives having an improved balance between tack, viscosity, bonding characteristics, and shear adhesion failure temperature (SAFT).



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ADHESIVE COMPOSITIONS CONTAINING MULTIBLOCK POLYISOPRENE-POLYSTYRENE COPOLYMERS AND ARTICLES INCLUDING SAME

BACKGROUND INFORMATION

1. Field of the Invention

In general, this invention relates to adhesive compositions constituted of multiblock polyisoprene-polystyrene block copolymers. In particular, it relates to pressure sensitive adhesives, especially pressure-sensitive, hot-melt adhesives formed from such block copolymers.

2. Background of the Invention

Low styrene, triblock polystyrene-polyisoprene-polystyrene copolymers are known to yield useful pressure sensitive adhesives (PSAs) when used in combination with, e.g., tackifier resins, plasticizer oils, and antioxidants. Such adhesives are useful in applications where good tack and an ability to bond to a wide variety of low- and high-energy surfaces, e.g., paper, plastic films, and metals, is required. Retaining tack and low temperature flexibility, good cohesive strength, and heat resistance while minimizing adhesive melt viscosity is very desirable. Generally, however, these properties cannot be optimized simultaneously.

Increasing tack by known techniques such as, for example, increasing the amounts of plasticizer oil and/or tackifier generally also results in decreased strength and heat resistance. On the other hand, increasing strength or heat resistance by increasing polymer content, or by using endblock-associating resins, generally raises viscosity and/or decreases tack.

Thus improving cohesive strength of such adhesives without adversely affecting tack, bonding characteristics, and heat resistance, as well as not increasing adhesive viscosity, remains desirable.

SUMMARY OF THE INVENTION

Briefly, the present invention provides a bimodal multiblock BABA copolymer. A represents a polystyrene block having a weight average weight (M_w) of from about 7,000 to about 30,000, and B represents a polyisoprene block having a M_w of from about 48,000 to about 120,000. The block copolymer has an overall M_w of from about 70,000 to about 150,000, an overall styrene content of from about 15 to about 50% (by wt.), and a Melt Index G of from 4 to 22 g/s. The bimodal multiblock BABA block copolymer can include one block copolymer having a M_w of from 50,000 to 140,000 and a second block copolymer having a M_w of from 100,000 to 250,000.

In another aspect, the present invention provides an article that includes a backing substrate and an adhesive layer on at least one major surface of the substrate. The adhesive layer is derived from a composition that includes a tackifying resin and the just-described bimodal multiblock BABA copolymer.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 displays a GPC graph of the BABA block copolymer used in Example 1.

DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

The present invention provides multiblock polyisoprene-polystyrene copolymers which, when formulated with tackifier resins, plasticizer oils, and antioxidants, produces PSAs, particularly pressure sensitive hot-melt adhesives having high cohesive strength.

PSAs must rapidly wet the surfaces to which they are to adhere. For good PSA performance, the overall adhesive mass must be soft, i.e., possess high creep compliance or low modulus. The multiblock copolymers of the present invention readily can be formulated to provide PSAs with good tack, adequate cohesive strength, and adequate heat resistance for most applications.

As previously stated, improving tack, particularly at low temperatures, can be accomplished by increasing the plasticizer oil or liquid resin content of the adhesive mass. However, doing so dilutes the styrene domains of the block copolymer, which leads to a loss in cohesive strength and heat resistance. In contrast, use of bimodal BABA block copolymers can provide improved cohesive strength without adversely affecting tack properties. Styrene content and overall molecular weight of the BABA block copolymer have been found to be key parameters for achieving a desired balance of properties in adhesive applications.

The BABA block copolymers of the present invention can be bimodal, having two block copolymers with different molecular weights. One block copolymer typically has a M_w of from 50,000 to 140,000, and the other typically has a M_w of from 100,000 to 250,000. These bimodal BABA copolymers provide tack development and low temperature flexibility in the PSA system as well as improved cohesive strength. They also maintain good heat resistance without adversely affecting tack properties.

The composition and molecular weight of the BABA block copolymer are important factors. The styrene domains stiffen (or raise the modulus of) the BABA block copolymer, and therefore increase the cohesive strength by providing a hard domain structure in the adhesive system. Although a monomodal BABA block copolymer often is too stiff (hard) to be used in a PSA system, a bimodal BABA block copolymer,

with its polyisoprene blocks contributing flexibility and compatibility, has been found to be optional.

Conjugated diene-monovinyl aromatic block copolymers useful in this invention are block copolymers derived from a monovinyl substituted aromatic compound and a conjugated diene. These include block copolymers such as BABA where A represents a polymerized monovinyl aromatic compound, usually styrene, and B represents a polymerized conjugated diene, usually 1,3-butadiene. The rubbery B block could be polybutadiene, a random or tapered styrene/ butadiene copolymer, polyisoprene, a random or tapered styrene-isoprene copolymer, or mixtures thereof. Presently preferred is butadiene and/or isoprene. Conjugated diene-monovinyl aromatic block copolymers of the present invention can be bimodal, which means that they have a molecular weight distribution with two peaks that may not be completely separated.

Fig. 1 displays a GPC graph of a BABA block copolymer (polyisoprene-styrene-polyisoprene-styrene) such as that used in Example 1. The two peaks between 15 and 20 minutes display the bimodal presence of different block copolymers having number average molecular weights (M_n) of 148,372 (first peak) and 77,387 (second peak). These copolymers, having resinous properties, contain from about 20 to about 40% (by wt.) polymerized styrene based on total weight of the copolymer. The remainder of the block copolymer is polymerized conjugated diene.

Basic preparation of useful monovinyl aromatic-conjugated diene block copolymers is disclosed in U.S. Pat. No. 2,975,160. The presently preferred bimodal block copolymers can be produced in accordance with U.S. Pat. Nos. 3,639,517 and 3,251,905. More specifically, they can be prepared by sequential charge copolymerization such as for example, that described in U.S. Pat. Nos. 4,584,346, 4,091,053, 4,704,434 and 4,704,435.

A PSA composition can be formed by admixing a bimodal BABA block copolymer with compatible primary tackifying resins, a plasticizer oil and/or secondary tackifying resin, and an antioxidant. The compatible primary tackifying resins with which the BABA block copolymers are admixed may be the same or different, but generally better results are obtained by the use of different primary tackifying resins in any given formulation.

Preferred PSA compositions can include, per 100 parts by weight (pbw) of bimodal BABA block copolymers, from about 80 to about 225 pbw, preferably from about 90 to about 180 pbw, of primary tackifying resins and from about 0 to about 100 pbw, preferably from about 0 to about 50 pbw, of the plasticizer oil and/or secondary tackifying resin. The blend also can contain from about 0.1 to about 2% (by wt.), preferably from about 0.5 to about 1.5% (by wt.), of an antioxidant.

Useful tackifying resins include hydrocarbon resins, synthetic polyterpenes, rosin esters, and natural terpenes that are at least somewhat solid at ambient temperatures and that soften or become liquid at temperatures ranging from about 70° to about 135°C, preferably from about 85° to about 120°C. Exemplary primary tackifying resins include compatible resins such as (1) natural and modified rosins such, for example, as gum rosin, wood rosin, tall oil rosin, distilled rosin, hydrogenated rosin, dimerized rosin, and polymerized rosin, (2) glycerol and pentaerythritol esters of natural and modified rosins, such, for example, as the glycerol ester of pale, wood rosin, the glycerol ester of hydrogenated rosin, the glycerol ester of polymerized rosin, the pentaerythritol ester of hydrogenated rosin, and the phenolic-modified pentaerythritol ester of rosin; (3) copolymers and terpolymers of natural terpenes, e.g., styrene/terpene and alpha methyl styrene/terpene; (4) polyterpene resins having a softening point, as determined by ASTM method E28-58T, of from about 80° to 150°C; the latter polyterpene resins generally resulting from the polymerization of terpene hydrocarbons,

such as the bicylic monoterpene known as pinene, in the presence of Friedel-Crafts catalysts at moderately low temperatures; also included are the hydrogenated polyterpene resins; (5) phenolic modified terpene resins and hydrogenated derivatives thereof such, for example, as the resin product resulting from the condensation, in an acidic medium, of a bicyclic terpene and a phenol; (6) aliphatic petroleum hydrocarbon resins having a Ball and Ring softening point of from about 70° to 135°C; the latter resins resulting from the polymerization of monomers consisting primarily of olefins and diolefins; also included are the hydrogenated aliphatic petroleum hydrocarbon resins; (7) aromatic petroleum hydrocarbon resins, and mixed aromatic and aliphatic paraffin hydrocarbon resins, and the hydrogenated derivatives thereof, (8) aromatic modified alicyclic petroleum hydrocarbon resins and the hydrogenated derivaties thereof, and (9) alicyclic petroleum hydrocarbon resins and the hydrogenated derivatives thereof. The preferred primary tackifier is dependent on the amount and relative amounts of the BABA block copolymer employed in the blend. The selection of a particular primary tackifier is thus dependent upon the specific copolymer employed, and the amount of the specific copolymer employed. Suitable secondary tackifying resins are those named species wherein the resin is a liquid at ambient temperature.

Various plasticizing oils are useful in the practice of this invention. The plasticizing oil can be used in place of or in combination with the secondary tackifier to reduce viscosity and improve tack properties. Plasticizing oils that have been found useful include olefin oligomers and low molecular weight polymers, as well as vegetable and animal oils and their derivatives. Petroleum-derived oils that can be employed are relatively high boiling materials containing only a minor proportion of aromatic hydrocarbons (preferably less than 30% and, more preferably, less than 15% by weight of the oil). The oligomers may be polypropylenes, polybutenes, hydrogenated polyisoprene, hydrogenated

polybutadiene, polypiperylene and copolymers of piperylene and isoprene, or the like a having a M_w between about 350 and about 10,000. Vegetable and animal oils include glyceryl esters of the usual fatty acids and polymerization products thereof.

Stabilizer or antioxidant to be used in accordance with the practice of this invention includes high molecular weight hindered phenols and multifunctional phenols such as sulfur and phosphorous-containing phenols. Hindered phenols are known to those skilled in the art and may be characterized as phenolic compounds that also contain sterically bulky radicals in close proximity to the phenolic hydroxyl group thereof. In particular, tertiary butyl groups generally are substituted onto the benzene ring in at least one of the ortho positions relative to the phenolic hydroxy group. The presence of these sterically bulky substituted radicals in the vicinity of the hydroxyl group serves to retard its stretching frequency and, correspondingly, its reactivity; this steric hindrance thus providing the phenolic compound with its stabilizing properties. Representative hindered phenols include 1,3,5-trimethyl-2,4,6-tris-(3,5-di-tert-butyl-4-hydroxybenzyl) benzene; pentaerythrityl tetrakis-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate; n-octadecyl-3-(3,5-di-tert-butyl-4-hydroxy-phenyl)-propionate; 4,4'-methylenebis-(2,6-tert-butylphenol); 4,4'-thiobis-(6-tert-butyl-o-cresol), 2,6-di-tertbutylphenol; 6-(4-hydroxyphenoxy)-2,4-bis(n-octylthio)-1,3,5-triazine; di-n-octadecyl-3,5-di-tert-butyl-4-hydroxy-benzylphosphonate; 2-(n-octylthio)-ethyl-3,5-di-tert-butyl-4-hydroxy-benzoate; and sorbitol.

The PSA composition can be formed by mixing the required components in molten state, or the components can be dissolved in a suitable hydrocarbon solvent, e.g., an aromatic hydrocarbon such as benzene, toluene, xylene or the like, or an aliphatic hydrocarbon such as hexane, heptane or the like. For example, the adhesive composition can be prepared by melt mixing the BABA block polymers with the primary tackifying resin(s), the secondary tackifying resin and/or plasticizing oil

and stabilizer, in any order or sequence, or these materials can be added together simultaneously to form the adhesive composition. In commercial practice, the primary tackifying resin(s) and the BABA copolymers, with or without the simultaneous addition of the secondary tackifying resin or plasticizing oil, and stabilizer, can be blended together at a sufficiently elevated temperature to form a fluid melt. For example, the BABA block copolymers can be blended with a solid compatible primary tackifying resin(s) and stabilizer at temperatures of from about 130° to about 200°C, preferably at from about 150° to about 180°C, to form a fluid melt. The secondary liquid tackifying resin or plasticizing oil then can be added to the melt.

PSAs can be mixed and coated as a hot melt mass, dissolved in and applied from hydrocarbon solvents, and applied to a backing substrate, e.g., paper, cloth, film, metal foil, tape or the like, by coating techniques conventionally used for this purpose in the adhesive tape industry. The adhesive may be coated on one or both sides of the substrate depending upon its intended use. These adhesives are particularly useful in tape and label applications, packaging, bookbinding and disposable applications. The adhesive compositions are particularly useful in, for example, the construction of a disposable articles comprised of polyethylene or polypropylene bonded to a tissue, non woven, polyethylene or polypropylene substrate, particularly disposable diapers and feminine hygiene products; or in packaging applications to bond a wide variety of high and low energy surfaces, i.e., paper, plastic, films, metals or the like. The BABA block copolymers are also useful as a component in asphalt applications for sealant products.

In the following non-limiting examples, all parts are given in parts per hundred parts of BABA block copolymers except as may otherwise be indicated. In conducting the following tests, the composition and properties of the bimodal BABA block copolymers which were prepared for making the adhesive compositions were determined by techniques a -

c (infra) and the performance characteristics of those same compositions were determined by test procedures d - f:

a. Styrene content of the experimental BABA block copolymers can be determined from proton NMR spectra. Samples were dissolved in a mixture of deuterated tetrachloroethane and tetrachloroethylene, and analyzed on a Bruker 90 MHz spectrometer. Styrene content was calculated from the spectra by the method of V.D. Mochel, *Rubber Chem. and Tech.*, **40**, 1200 (1967).

b. Molecular weight of the BABA block copolymers was determined by GPC, using the method described by J.R. Runyon et al., *J. Poly. Sci.*, **13**, 2359 (1969).

c. Melt viscosities were measured at temperatures of -300°, 325°, 350° and 400°C, using a Brookfield Thermosel™ viscometer. See ASTM D-3236.

d. Shear Adhesion Failure Temperature (SAFT) is a measure of the ability of a bond to withstand an elevated temperature rising at 11.25°F/15 min (0.0069°C/s), under a constant force which pulls the bond in the shear mode. Bonds 1 inch by 1 inch (2.5 cm x 2.5 cm) are formed between an adhesive on a metallized polyester backing and a stainless steel panel, using a 4.5 lb. (2 kg) rubber roller. The panel is suspended vertically in an oven at 25°C and allowed to come to equilibrium. A 500 g weight is suspended from the free end of the adhesive tape, and the temperature is raised at the prescribed rate. The temperature at which the tape and weight fall from the panel is recorded. SAFT is reported as the average of three such determinations.

e. 180° Peel Adhesion of the adhesives is determined according to the procedures outlined in PSTC-1 of the Pressure Sensitive Tape council. A 1 inch by 6 inch (2.5 cm

x 15.2 cm) strip of adhesive tape (on a 0.05 mm metallized polyester backing) is applied to a stainless steel (SS), polyethylene (PE) or polypropylene (PP) panel with a 4.5 lb. (2 Kg) rubber roller. The tape is peeled back over itself at 180° in a tensile tester at a constant crosshead speed of 12 in/min (0.51 cm/s). The average force required to peel the tape from the panel is recorded. The 180° peel adhesion value is reported as the average of two or three such determinations.

f. Quick Stick is that property of a PSA that causes it to adhere instantly to a surface, using no external pressure, to secure a thorough bond. This method is described in PSTC-5. Quick stick is measured as the force resisting peeling of a tape at 90° from a standard surface upon which it has been applied under no other pressure than the weight of the tape itself. Quick Stick is measured using a tensometer with a crosshead speed of 12 in/min (0.51 cm/s). The Quick Stick is reported as the average of two or three determinations.

EXAMPLES

The adhesive formulations designated 1-3 below utilized SR-8300 BABA block copolymer SR-8300 (Firestone Synthetic Rubber Co.; Akron, Ohio), ESCOREZ™ 1310 primary tackifying resin, Shellflex™ 371 plasticizer, and IRGANOX™ 1010 stabilizer. This bimodal BABA block copolymer had an overall M_w of 120,000, a styrene content of 20% by weight, and Melt Index G of 13 g/s.

The comparative adhesive formulations A-C utilized Kraton™ 1107 ABA block copolymer, ESCOREZ™ 1310 tackifying resin, Shellflex™ 371 plasticizer, and IRGANOX™ 1010 stabilizer. The Kraton™ 1107 S-I-S

block copolymer had an overall M_w of 115,000, a styrene content of 17% by weight, and a Melt Index G of 13 g/s.

Table 1 summarizes and identifies the properties of the formulated adhesive compositions.

Table 1

	1	A	2	B	3	C
Block copolymer (g)	106.5	106.5	35.5	35.5	35.5	35.5
Tackifying resin (g)	149.1	149.1	49.7	49.7	49.7	49.7
Plasticizer (g)	42.6	42.6	14.2	14.2	14.2	14.2
Stabilizer (g)	1.8	1.8	0.6	0.6	0.6	0.6
Toluene (g)	-	-	100	100	-	-
Viscosity (cP)						
at 149°C	140,750	8,850	-	-	51,500	13.350
at 163°C	43,500	33,450	-	-	17,060	7,975
at 177°C	16,125	14,625	-	-	6,575	5,287
at 204°C	3,840	4,975	-	-	1.675	2,687
Gardner Color	-	-	-	-	8	12
Cohesive Tensile (kPa)	-	-	-	-	283.2	288.8
Adhesive Tensile (kPa)	848	674	-	-	-	-
Peel Adhesion (g/cm)						
90° Quick Stick	-	-	563	522	538	521
180° Peel, SS	-	-	808	716	861	830
180° Peel, PE	-	-	476	403	503	496
180° Peel, PP	-	-	574	618	686	651
SAFT (°C)	-	-	92.2	93.3	86.1	89.4
Rolling Ball (cm)	-	-	0.16	0.16	0.64	0
Polyken Tack (g)	-	-	>1000	940	975	965
Thickness (μm)	-	-	-	-	2.3	3.0
Coat Weight (g)	-	-	0.235	0.228	-	-

As is evident from the results of Table 1, adhesive formulations utilizing the multimodal block copolymers of the present invention

displayed a better overal range of properties than the formulations using the comparative bimodal coupled S-I-S copolymer.

Adhesive compositions having good tack and high cohesive strength are useful in many PSA applications such as tapes and labels. The adhesive compositions can be coated from the melt or from solution onto various substrates such as paper or plastic films such as polyester, polypropylene, polyethylene, etc., or foam such as polyurethane, polystyrene, etc. The adhesive compositions of this invention as exemplified by Examples 1 through 3 clearly are superior to an adhesive composition prepared from ABA block copolymers.

The polyisoprene-polystyrene-polyisoprene-polystyrene or BABA block copolymers described herein may be prepared using any of the well-known anionic polymerization synthesis techniques for preparing linear styrenic block copolymers.

Various modifications and alterations that do not depart from the scope and spirit of this invention will become apparent to those skilled in the art. This invention is not to be unduly limited to the illustrative embodiments set forth herein.

CLAIMS

We claim:

1. A composition comprising a bimodal multiblock BABA copolymer wherein

A represents a polystyrene block having a weight average weight of from about 7,000 to about 30,000, and

B represents a polyisoprene block having a weight average molecular weight of from about 48,000 to about 120,000,

said block copolymer having an overall weight average molecular weight of from about 70,000 to about 150,000, an overall styrene content of from about 15 to about 50 weight percent, and a Melt Index G of from 4 to 22 g/s, said bimodal multiblock BABA block copolymer comprising one block copolymer having a weight average molecular weight of from 50,000 to 140,000 and another block copolymer having a weight average molecular weight of from 100,000 to 250,000.

2. The composition of claim 1 wherein the overall styrene content of said copolymer is from about 20 to about 40 weight percent.

3. The composition of any of claims 1 to 2 wherein the Melt Index G is from 10 to 15.

4. An article comprising a backing substrate and, having on at least one major surface of said substrate, a layer of an adhesive composition comprising a tackifying resin and a bimodal multiblock BABA copolymer wherein

A represents a polystyrene block having a weight average weight of from about 7,000 to about 30,000, and

B represents a polyisoprene block having a weight average molecular weight of from about 48,000 to about 120,000,

said block copolymer having an overall weight average molecular weight of from about 70,000 to about 150,000, an overall styrene content of from

about 15 to about 50 weight percent, and a Melt Index G of from 4 to 22 g/s, said bimodal multiblock BABA block copolymer comprising one block copolymer having a weight average molecular weight of from 50,000 to 140,000 and another block copolymer having a weight average molecular weight of from 100,000 to 250,000.

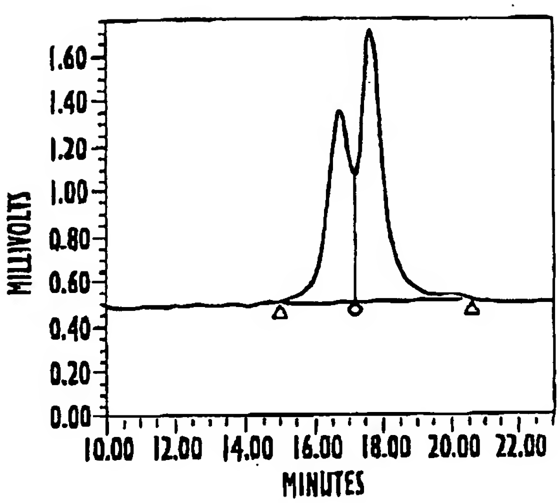
5. The article of claim 4 wherein the overall styrene content of said copolymer is from about 20 to about 40 weight percent.

6. The article of any of claims 4 to 5 wherein the Melt Index G is from 10 to 15.

7. The article of any of claims 4 to 6 wherein said backing substrate comprises paper, cloth, plastic, film, metal foil, form, or tape.

8. The article of any of claims 4 to 7 wherein said bimodal multiblock BABA copolymer comprises one block copolymer having a weight average molecular weight of from 50,000 to 140,000 and another block copolymer having a weight average molecular weight of from 100,000 to 250,000.

9. The article of any of claims 4 to 8 wherein said adhesive composition is applied to both major surfaces of said substrate.


MILLIVOLTS
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18.00
20.00
22.00
MINUTES

FIG.1

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/08012

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08F297/04 C09J153/02 B32B27/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08F C09J B32B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3 639 517 A (KITCHEN ALONZO G ET AL) 1 February 1972 (1972-02-01) cited in the application claims	1-3
Y	US 3 251 905 A (ROBERT P ZELINSKI) 17 May 1966 (1966-05-17) cited in the application claims	1-3
A	US 5 773 521 A (HOXMEIER RONALD JAMES ET AL) 30 June 1998 (1998-06-30) the whole document	1-9
A	US 5 554 697 A (VAN DIJK MENNO A ET AL) 10 September 1996 (1996-09-10) the whole document	4-9

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
29 June 2000	10/07/2000

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 773 506 A (MA JINGJING ET AL) 30 June 1998 (1998-06-30) ————	4-9

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 00/08012

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